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(54) DETERGENT BARS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to non-soap detergent bars, by which is meant bars based on non-soap detergents, for personal washing, and to processes for their preparation.

Non-soap detergent bars consist essentially of a non-soap detergent-active substance, a binder to hold the bar together and a plasticiser to make the material of the bar plastic enough to be shaped by plodding. Soaps are commonly used as plasticisers in a non-soap detergent bar. The bars commonly also contain superfatting agents, softening agents and fillers. The function of a superfatting agent is to give the bar improved lathering properties. Among the superfatting agents commonly used in a non-soap detergent bar are free higher fatty acids, which also act as binders and plasticisers.

It has now been discovered that by converting some or all of the free fatty acids into an inclusion compound with urea known as a clathrate, the lathering properties are improved, particularly in respect of lather volume.

British Patent 1,163,925 describes the preparation of soap bars based on compositions containing 35—60% of urea and 7—15% of fatty acid by weight which are heated to form an inclusion compound, and mention is also made of including a minor proportion of a non-soap detergent. In the present invention much less urea is incorporated for the improved lathering properties.

Clathrate compounds between C₈—C₂₂ fatty acids and urea are well known: irrespective of the precise length of the fatty acid chain, a loose association is formed between about 3 parts by weight of urea and 1 part of free fatty acid. Where a non-soap detergent bar is prepared containing urea and free fatty acid, the clathrate with that 3:1 ratio is present in the bar even where the clathrate is not formed before incorporation into the detergent

compositions, because the normal conditions of detergent bar production can provide intimate mixing sufficient to form clathrate from urea and free fatty acid added independently. Where more or less than the equivalent of urea to free fatty acid required for the clathrate is incorporated, the excess of one component over the other can be regarded as remaining in the free state. In this specification the clathrate together with any excess of one component over the other are expressed as the total of urea and free fatty acid present.

The present invention provides a superfatted detergent bar comprising a non-soap detergent and a clathrate of urea and a free C₈—C₂₂ fatty acid, in which the amount of urea, and the total amount of urea and free fatty acid present are less than 25% and no more than 50%, respectively, by weight of the total active detergent, urea and free fatty acid present, and the amount of non-soap detergent is at least 10% by weight of the total active detergent.

The amount of non-soap detergent is preferably at least 50%, and especially at least 60% or 70% of the total active detergent present. The total amount of urea and free fatty acid present is preferably from 1 to 45% and especially from 5 to 40% by weight of the total active detergent, urea and free fatty acid. The amount of total active detergent thus expressed is on a dry-weight basis, it being understood that a non-soap detergent bar necessarily contains a sufficient amount of water as well as plasticisers to give the plastic qualities that are required for a bar. This amount of water varies according to the chemical composition of the bar, but is generally within the range of from 2 to 15% by weight of the bar.

The amount of free fatty acid by weight of the total active detergent can be within the range from 1 to 50% and is preferably 3 to 45%: and by weight of the total active detergent, urea and free fatty acid is preferably less than 30%, especially less than 25%. Preferably the detergent bar has less than 20% of urea by weight of the total active detergent, urea and free fatty acid. The clathrate can be provided by from 0.1 to 10 parts of urea for each part by weight of free fatty acid. The

bar preferably has from 0.1 to 6, and especially from 0.1 to 3.5, parts by weight of urea for each part of the free fatty acid. Advantageously the amount of urea is not more than that required to form clathrate from all the free fatty acid present.

Detergent bars includes both billets, which are obtained by cutting the detergent composition extruded from an orifice, and tablets, which are shaped by stamping.

As is well known to those skilled in detergent bar manufacture, the bar ingredients, including active detergents, binders, plasticisers, superfatting agents and fillers, require to be chosen in such a way that a plastic bar can be prepared from them.

The non-soap active detergent in the detergent bars of the invention can be chosen from a wide variety of substances, alone or in combination. Examples of suitable non-soap detergent-active compounds are fatty alcohol sulphates, such as those derived from C_{10} to C_{18} alcohols, especially lauryl and myristyl alcohol; fatty acid derivatives including fatty acid monoglyceride sulphates, fatty acyl sarcosinates, fatty acyl isethionates and fatty acid sulphonates, such as those derived from C_{10} to C_{22} fatty acids, especially lauric, myristic, palmitic and stearic acids; alkane and α -olefin sulphonates, such as those derived from C_{10} to C_{22} alkanes and olefins, especially from mixtures of C_{11} to C_{18} alkanes or α -olefins; and sulphonated alkyl mono- and poly-glycerol ethers, such as those derived from C_{10} to C_{18} fatty alcohols. The cation in these non-soap detergent-active compounds is normally sodium or potassium, but other ions may be present, for instance ammonium, substituted ammonium or magnesium cations. The preparation of detergent bars from such non-soap detergents, with or without soap, is described in British Patents 756,502, 1,151,052, 1,167,131, 1,171,616, 1,171,617, 1,185,317, 1,281,895, 1,295,275 and US Patents 2,894,912, 3,024,273, and 3,070,547.

Where soap is present, it can be provided by alkali metal, ammonium or substituted ammonium salts, preferably sodium or potassium salts, of long-chain fatty acids. Normally such fatty acids will be straight chain saturated or unsaturated fatty acids of from 8 to 22 carbon atoms. Suitable such fatty acids are the fatty acids of tallow, groundnut, cottonseed, palm, palm kernel, babassu, and coconut oils, for instance lauric, myristic, palmitic, oleic, and stearic acids and the acids of dehydrated hardened castor oil; or erucic and behenic acids. Typical mixtures of such acids suitable for the formation of soaps are, for example, mixtures containing from 30 to 95% by weight of tallow fatty acid and from 70 to 5% by weight of coconut oil fatty acid, and especially from 40 to 80% tallow fatty acid and from 60 to 20% coconut oil fatty acid. A suitable proportion of a relatively soft soap,

for instance soap derived from an unsaturated fatty acid such as oleic acid, or a potassium soap rather than a sodium soap, can improve the capacity of the soap to act as a plasticiser in a non-soap detergent bar. All soap that is present forms part of the total active detergent irrespective of its function as plasticiser.

The general structural requirements for a fatty acid to form a urea clathrate are well-known, and whether any unusual fatty acid will form a urea clathrate is easily tested. The presence of a urea-fatty acid clathrate in a urea-free fatty acid composition or a detergent bar can normally be detected from X-ray powder diffraction diagrams which show the short spacings characteristic of a urea-fatty acid clathrate. The fatty acid employed to form the clathrate can be any free fatty acid capable of forming a clathrate, such as one of the above-mentioned fatty acids, or mixtures of them. It will normally be straight-chain and saturated or monoethenoid. The free fatty acid in the clathrate can have the same composition as that of soap present, or it can be different. Coconut oil fatty acid is particularly suitable for use in providing the clathrate. Although the metal ions of active detergent present in a detergent, particularly soap, can exchange within the individual detergent compounds or be transferred to free fatty acid added to the bar composition, it is convenient to treat any free fatty acid added either before or during the formation of the bar as not exchanging ions with detergent compounds present.

The bars can contain moisturising compounds, such as disodium adipate, sodium malate or sodium lactate, and others described in British Patents 1,417,183 and 1,460,442 and German Patent Specification DTOS 2,337,342, and the use of the clathrates with such moisturisers is particularly valuable, for such bars containing them have a tendency to exhibit reduced lathering properties. The amount of moisturising compound used will generally be from 5 to 15% by weight of the total active detergent, urea and free fatty acid present. Suitable softening agents for use in the bars are fatty alcohols, for instance myristyl, cetyl and stearyl alcohols. Detergent bars of the invention can also contain sequestering agents, antioxidants, opacifiers, fluorescers and colourants.

In a process of the invention a detergent bar is made by incorporating in a detergent bar composition the required urea and free fatty acid under conditions to provide the clathrate, and forming the composition containing clathrate into a bar. The pre-formed clathrate, made for instance by heating together the urea and free fatty acid, can be dispersed in the total active detergent or the soap; preferably it is dispersed in the dried detergent composition by milling. Alternatively the clathrate is formed in the total active deter-

gent or soap *in situ*. Wet soap (having more than 15% of water) containing urea and free fatty acid can be heated and then dried to form the clathrate. For instance the free fatty acid can be mixed with a neutral wet soap base containing the urea before drying and the heated liquid mixture passed through a conventional vacuum dryer, during which the clathrate is formed. The clathrate can also be formed *in situ* in the detergent composition by dispersing the urea and free fatty acid by milling: preferably the free fatty acid is dispersed in the composition already containing the urea. The urea is conveniently added as a fine powder and the fatty acid is conveniently added in the molten state, in order to promote dispersion. Adequate heating for formation of the clathrate can occur during a normal process of milling and plodding where the fatty acid has a melting point below processing temperature. The composition to which the clathrate is added or in which it is formed should of course be free of alkali.

The invention is illustrated by the following Examples, in which all amounts are by weight and temperatures are in °C. The contents % of ingredients in the bars are given as amounts % of total active detergent, free fatty acid and urea.

The procedure of the lather volume test was as follows.

Lather volume test

In this test a tablet is used by operators wearing thin rubber gloves to generate lather, simulating conditions of consumer use, according to a standard procedure using water of standard hardness at a standard temperature. A tablet which has been washed down well at least 10 minutes before the test is wetted and twisted 15 times between the hands in such a way that it turns over each time; the tablet is then set down and lather is generated from the liquor on the hands by rubbing the tips of the fingers of the left hand on the palm of the right hand 10 times forwards to the finger-tips and back. The lather on the right hand is then collected by gripping above the wrist with the left hand and squeezing while moving it over the fingers, thus transferring the lather to between the forefinger and thumb of the left hand. The gripping and squeezing is repeated on the left hand using the right. This process of collection is repeated 5 times, leaving the lather collected on the right hand. This lather is collected with the fingers of the left hand and placed again in the palm of the right hand. The whole procedure of rubbing and collecting is repeated once again. The step of forming and collecting the lather

should take about 30 seconds. The collected lather is placed in a beaker and the hands are then rinsed.

Two more batches of lather are made by the above procedure, and the combined lather in the beaker is gently stirred with a glass rod to release any large pockets of trapped air, the surface smoothed off with the fingers and the lather volume measured.

Each test is made in duplicate, and the results are averaged.

EXAMPLES 1 and 2

A non-soap detergent composition having the following ingredients was used as a base composition.

	Parts %	
Sodium acylisethionate	48.6	75
Sodium dodecylbenzene sulphonate	2.0	
Sodium soap	11.0	
Coconut oil fatty acid	3.0	
Stearic acid	21.7	80
Miscellaneous ingredients including inorganic salts, titanium dioxide, colouring matter and perfume	8.5	
Water	5.2	85

The sodium acylisethionate was one whose acyl group was that of the fatty acids from coconut oil and the sodium soap was a mixture of soaps derived from stearic acid and the fatty acids of tallow and coconut oil.

To 100 parts of the base composition was added 3.9 parts of urea and the mixture milled and plodded in conventional equipment, cut into billets and stamped into tablets (Example 1). The tablets contained 56.1% of non-soap detergent, 12.2% of soap, 27.4% of free fatty acid and 4.3% of urea as clathrate (5.8%).

To a further 100 parts of the base composition was added 12.6 parts of urea and tablets were prepared in the same way (Example 2), containing 51.2% of non-soap detergent, 11.1% of soap, 25.0% of free fatty acid and 12.7% of urea as clathrate (17.0%).

Tablets (A) were also prepared from the base composition and contained 58.6% of non-soap detergent, 12.7% of soap, and 28.6% of free fatty acid.

All tablets were then submitted to the lather volume test, with the following results.

Tablets	Lather Volume		
	at 20°	at 40°	
Example 1	868	700	
Example 2	800	762	
A	568	612	110

EXAMPLES 3 and 4

A non-soap detergent composition having the following ingredients was used as a base composition for the preparation of tablets.

	Parts %
5 Sodium C ₁₁ —C ₁₄ alkane sulphonate	22.1
Sodium C ₁₅ —C ₁₈ alkane sulphonate	29.4
10 Sodium C ₁₆ —C ₁₈ α-olefin sulphonate	22.1
Myristyl alcohol	6.3
Cetyl alcohol	5.0
Stearyl alcohol	5.0
15 Miscellaneous ingredients, including inorganic salts, titanium dioxide and colouring matter	5.2
Water	4.9

- 20 To 100 parts of the base composition was added 5.2 parts of a clathrate prepared from 3.9 parts of urea and 1.3 parts of coconut oil fatty acid by mixing and heating the components together at 90° in the presence of a trace of water and cooling, together with 2.6 parts of additional free coconut oil fatty acid. The mixture was milled, plodded, cut into billets and stamped into tablets (Example 3), containing 90.4% of non-soap detergent, 4.8% of free fatty acid and 4.8% of urea as clathrate (6.4%).

- 25 To a further 100 parts of the base composition was added 17.0 parts of the urea coconut oil fatty acid clathrate derived from 12.75 parts urea and 4.25 parts fatty acid, and tablets were prepared as before (Example 4), containing 81.2% of non-soap detergent, 4.7% of free fatty acid and 14.1% of urea as clathrate (18.8%).

- 30 Tablets (B) were also prepared from 100 parts of the base composition and 3.75 parts of free coconut oil fatty acid: the tablets contained 95.0% of non-soap detergent and 5.0% of free fatty acid.

- 35 All tablets were then submitted to the lather volume test, with the following results.

	Lather Volume	
	at 20°	at 40°
Tablets		
Example 3	625	662
50 Example 4	600	725
B	525	512

EXAMPLES 5 and 6

- A non-soap detergent composition having the following ingredients was used as a base composition.

	Parts %
Disodium salt of a sulphonated hardened tallow fatty acid	27.6

Disodium salt of a sulphonated coconut oil fatty acid	14.6	
Sodium C ₁₁ —C ₁₈ alkyl sulphate	28.1	
Myristyl alcohol	11.1	65
Miscellaneous ingredients including inorganic salts titanium dioxide and colouring matter	7.3	
Water	11.3	70

To 100 parts of the base composition was added 5.8 parts of a clathrate prepared from 4.35 parts urea and 1.45 parts of a hardened tallow fatty acid by mixing and heating the components together at 90° in the presence of a trace of water and cooling, together with 10.1 parts of free hardened tallow fatty acid, and the mixture milled, plodded, cut into billets and stamped into tablets (Example 5) containing 81.6% of non-soap detergent, 13.4% of free fatty acid and 5.0% of urea as clathrate (6.7%).

To a further 100 parts of the base composition was added 19.0 parts of the hardened tallow fatty acid clathrate and 7.9 parts of free hardened tallow fatty acid, and tablets prepared as before (Example 6), containing 72.3% of non-soap detergent, 15.0% of free fatty acid and 14.7% of urea as clathrate (19.6%).

Tablets (C) were also prepared from 100 parts of the base composition and 11.1 parts of the free hardened tallow fatty acid: the tablets contained 85.4% of non-soap detergent and 13.6% of free fatty acid.

All tablets were then submitted to the higher volume test, with the following results.

Tablets	Lather Volume	
	at 20°	at 40°
Example 5	738	638
Example 6	825	750
C	638	575

WHAT WE CLAIM IS:—

1. A superfatted detergent bar comprising a non-soap detergent and a clathrate of urea and a free fatty acid, in which the amount of urea, and the total amount of urea and free fatty acid present are less than 25% and not more than 50%, respectively, by weight of the total active detergent, urea and free fatty acid present, and the amount of non-soap detergent is at least 10% by weight of the total active detergent.

2. A detergent bar according to Claim 1, in which the amount of non-soap detergent is at least 50% by weight of the total active detergent.

3. A detergent bar according to Claim 2, in which the amount of non-soap detergent is at least 70% by weight of the total active detergent.

4. A detergent bar according to any preceding claim, in which the total amount of urea and free fatty acid is from 5 to 40% by weight of the total active detergent, urea and free fatty acid. 20
5. A detergent bar according to any preceding claim, which contains from 0.1 to 3.5 parts by weight of urea for each part of free fatty acid. 25
6. A detergent bar according to any preceding claim, in which the non-soap detergent comprises a fatty acyl isethionate. 30
7. A detergent bar according to any preceding claim, in which the free fatty acid comprises coconut oil fatty acid.
8. A detergent bar according to Claim 1, substantially as described in any one of Examples 1 to 6.
9. A process for making a detergent bar according to any preceding claim, which comprises incorporating in a detergent bar composition the required urea and free fatty acid under conditions to provide the clathrate, and forming the composition containing clathrate into a bar.
10. A process according to Claim 9, in which the pre-formed clathrate is dispersed in the dried detergent composition by milling.
11. A process for making a detergent bar according to Claim 1, substantially as described in any one of Examples 1 to 6.
12. A detergent bar when prepared by a process according to any one of Claims 9 to 11.

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